

Study on Pyrolysis and Environmental Protection of Corn Stalk in Thermal Expansion Cracking Agent

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Abstract. The thermal expansion cracking agent is a new type of cracking stone, which is made of straw, coal gangue, carbon black, calcium peroxide and so on. After mixing, it is made by crushing, kneading, granulation and drying. Among them, the environmental protection of straw in the application of thermal expansion cracking agent cannot be ignored. This article discusses the pyrolysis process of straw in the thermal expansion rip cracking agent and the migration and transformation mechanism of pollutant elemental sulfur. The results show that Al_2O_3 can be used as the main component of coal gangue in the combustion process of thermal expansion cracking agent. Al_2O_3 can prevent sulfur in the straw from decomposition and discharge into the air with high-temperature combustion of thermal expansion cracking agent, thus ensuring the use of thermal expansion cracking agent is environmentally friendly.

1. Introduction

China has abundant straw resources. Compared with fossil fuels, straw has a relatively low carbon content, a relatively high content of hydrogen and oxygen, a relatively high volatile content, and a lower calorific value than coal. Straw has good environmental friendly properties and low sulfur and nitrogen pollution. Thermal expansion cracking agent is a new type of cracked stone product that is safe and environment-friendly and can be quickly cracked. It uses the concept of comprehensive utilization of mineral waste gangue and plant stalks. The thermal expansion cracking agent is made of straw, coal gangue, coal-based carbon black, calcium peroxide, etc., and after being proportioned, it is made by crushing, kneading, granulating, and drying processes. The composition and preparation process of thermal expansion cracking agent, mine explosive and static cracking agent are completely different. Among them, coal gangue is a solid waste discharged during the coal mining process and coal washing process [1-3]. It is a black-gray rock with low carbon content and harder than coal, which is associated with the coal seam during the coal formation process. Its main component is Al_2O_3 , SiO_2 , and includes certain Fe_2O_3 , CaO , MgO , Na_2O , K_2O , P_2O_5 , SO_3 and trace rare elements.

With the concept of domestic ultra-low emission, the environmental pressure continues to increase, and the environmental protection issues of straw in the application of thermal expansion cracking agent cannot be ignored. Further attention and discussion will be made on the mechanism of nitrogen and sulfur desorption and conversion in the pyrolysis process of straw in thermal expansion cracking agent, which has a high guiding significance for the popularization and application of thermal expansion cracking agent.



2. Corn straw and its common combustion

China's corn has a large area and is widely distributed. It is a country where corn grows throughout the year. From Heilongjiang Province in the north, to Hainan Province in the south, there is corn planting. Among them, Heilongjiang, Jilin, Liaoning, Hebei, Shandong, Shanxi, Henan, Shaanxi, Sichuan, Guizhou, Yunnan, and Guangxi are the main producing areas.

Corn stalk is a kind of cellulosic biomass composed mainly of cellulose, hemicellulose and lignin. The contents were 42.4%, 29.6%, and 21.7%, respectively. Among them, cellulose is a linear polymer made of β -(1 $\rightarrow$ 4)-D-pyranoglucosyl groups linked by β -glycosidic bonds between the 1st and 4th positions of adjacent sugar units ($C_6H_{10}O_5$)_n; unlike cellulose, hemicellulose is an inhomogeneous polysaccharide composed of many kinds of glycosyl units. The structural units that make up hemicellulose mainly include D-xylosyl, D-mannosyl, D-glucosyl, D-Galactosyl, L-arabinose, and 4-O-methyl-D-glucuronyl, etc.; Lignin is a complex polymer compound composed of guaiacyl, syringyl, and p-hydroxyphenyl structural units linked by C-C bonds and C-O-C ether bonds. The main elements contained in corn stover are carbon, hydrogen, oxygen, nitrogen and sulfur. The results of elemental analysis are shown in Table 1.

Table 1. Main elements content of corn stalk (%)

Chemical Components	The main element content (%)				
	C	H	O	N	S
Corn stalks [4]	41.87	5.95	52.53	0.11	0.07
Corn stalks [5]	42.96	5.81	34.47	2.00	0.22
Corn stalks [6]	44.54	5.85	42.83	0.57	0.48

As can be seen from Table 1, the three elements of C, H and O account for more than 97% of the total element content of corn stalk. Therefore, when the corn stalk is burned normally, it is mainly the physical and chemical reactions of three elements of C, H and O. The process is as follows: the straw is heated to decompose and gasify low-molecular-weight substances, and volatiles are precipitated, mainly including CO, H₂, CO₂, CH₄, and C_nH_m. After reaching the ignition temperature, the volatiles form a gas-phase combustion flame and high temperature, and the inner layer volatiles of the straw are further precipitated and burned rapidly in a short period of time, resulting in a rapid increase in the amount of heat released. After the volatile components are burned, the coke is disintegrated.

The two elements of S and N in corn stalk are the main elements except the three elements of C, H and O. Although the content is small, for example, the sulfur content in straw is only 1/2 to 1/3 of the content of sulfur in coal. It is a relatively clean fuel [7], but taking into account that sulfur is combustible, sulfur dioxide and sulfur trioxide that are generated by combustion are harmful substances. Although nitrogen is not flammable, it can be converted to nitrogen oxides, which is also a pollutant. Therefore, S, N elements are still the main elements of straw combustion pollution. The S element contained in the straw comes from the sulfate in the soil and absorbs into the plant body through the root and participates in the plant cell composition. It can be divided into organic sulfur and inorganic sulfur. When burning, organic sulfur can decompose with the volatiles when it is lower than 500°C, and the inorganic sulfate decomposes to generate SO₂ at a higher temperature. During the combustion process, nitrogen compounds in the straw are thermally decomposed. Gas-phase nitrogen and tar nitrogen are precipitated along with the remaining volatile components of the straw. Gas-phase nitrogen includes HCN, NH₃, and a small amount of HNCO. As the temperature increases, tar nitrogen will be further cracked into HCN. NH₃ and HNCO are oxidized to NO, and NO is reduced to N₂ in the presence of excess carbon black.

It is worth noting that in addition to the production of sulfur oxides and nitrogen oxides during the combustion of corn stover, the trace elements chlorine and potassium in the straw are also two elements worthy of attention in the process of burning straw. Among them, chlorine is one of the essential elements of plants and plays an important role in photosynthesis, cell division, osmotic adjustment, and charge balance. Plants absorb chlorine in the form of ions, which exist mainly in the

form of ions in plants. In the biomass and coal pyrolysis, combustion and gasification processes, chlorine is released into the gas phase and the temperature is concentrated at 200-400°C. The main release forms are hydrogen chloride and alkali metal hydrides such as NaCl, KCl, HCl and Cl₂. Potassium is the alkali metal element with the highest content in straw, and it is very lively. It is easily precipitated in the process of combustion and utilization [8]. It is especially harmful in boiler combustion.

3. Pyrolysis process of straw in thermal expansion cracking agent

The pyrolysis mechanism of straw in the thermal expansion cracking agent is different from the ordinary combustion, so it is necessary to study and discuss. The reason is that the ordinary combustion of straw belongs to the semi-open combustion system. The oxygen element needed for combustion is not only from the straw itself, but also can be obtained from the air in large quantities. In the thermal expansion cracking agent, the pyrolysis of the straw belongs to the closed system combustion, the combustion pressure is higher than the ordinary combustion, and the combustion environment is the other component of the thermal expansion cracking agent. The required oxygen source comes from the thermal expansion cracking agent itself. The above-mentioned difference in combustion environment causes differences in pyrolysis products, pyrolysis rate, release of harmful gases, and other common pyrolysis products of the corn stover in the thermal expansion cracking agent.

For the thermal expansion cracking agent, its composition mainly includes calcium peroxide, carbon black, straw and coal gangue. The raw materials of the components are all powdery, and are fully mixed in the preparation process. Among them, calcium peroxide is an oxidant component that provides the most important source of oxygen; Straw and carbon black are combustion components that provide the elements needed for combustion; Coal gangue belongs to the buffer protection component, in the expansion of the combustion space, buffer combustion pressure at the same time, in order to avoid oxidation and reduction reactions to produce harmful substances to provide protection. According to research, the pyrolysis process of corn stover in thermal expansion cracking agent is divided into the following steps:

- 1) Under the action of ignition and high temperature, calcium peroxide decomposes to generate oxygen and forms oxygen radicals at high temperatures; At the same time, the straw is decomposed by heat to release gas volatiles, which produces a certain pressure in a closed borehole environment. The pressure promotes the gas volatiles to rapidly mix with oxygen and oxygen radicals in the gaps of the solid body of the thermal expansion lithogenerator to form primary combustion.

- 2) The high temperature formed by primary combustion further promotes faster decomposition and combustion of calcium peroxide and straw, resulting in higher temperature and pressure, promoting the start of combustion of carbon black, and promoting the initial activation and decomposition of some coal gangue surfaces;

- 3) The entire system enters the combustion peak, the temperature and the system pressure reach the maximum, the stable gas produced by the combustion continues to provide pressure, the unstable gas generated by the combustion reacts further, or reacts with the solid substance such as the coal gangue component. At this point the matrix of thermal expansion cracking agent is severely decomposed, and coal gangue is the main solid component in the system, buffering the gas pressure in the combustion space.

- 4) The fuel is gradually depleted. With the thermal expansion cracking agent doing external work, the temperature and pressure of the system are rapidly reduced and the combustion is completed. The gas products generated by the thermal expansion cracking agent are discharged into the atmosphere, and the solid phase products remain in the rock boreholes.

4. Application of straw in thermal expansion cracking agent environmental protection

The environmental issue of the combustion products of straw in the thermal expansion cracking agent is the key issue that determines whether the process of thermal expansion cracking agent is green.

From the above research, we can see that the main pollutants produced during the ordinary combustion process of straw are sulfur oxides and nitrogen oxides. Therefore, the study of the migration of sulfur elements in thermal expansion cracking agents is the key to whether straw is environmentally friendly in thermal expansion cracking agents.

The sulphate in the straw, such as CaSO_4 , is the main source of sulfur. Suppressing sulfate decomposition during the operation of the thermal expansion cracking agent is the key to preventing the emission of sulfur. Studies have shown that [9], Al_2O_3 can effectively inhibit the sulfur decomposition product CaSO_4 pyrolysis, sulfur fixation. At the same time, Al_2O_3 can also interact with CaSO_4 and CaO to form double-salt $\text{CaSO}_4 \cdot 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ with higher thermal stability, which is encapsulated on the surface of CaSO_4 crystal, thereby inhibiting the decomposition of CaSO_4 . Al_2O_3 is the main component of coal gangue. Therefore, coal gangue also acts as a protective agent in the thermal expansion cracking agent, preventing the sulfur element in the straw from being decomposed and discharged into the air with the high-temperature combustion of the thermal expansion cracking agent.

5. Conclusions

The environmental issue of the combustion products during the use of thermal expansion cracking agent determines whether the application process of thermal expansion cracking agent is green. The key to its research lies in the migration path of sulfur element in thermal expansion cracking agent. Studies have shown that sulfates such as CaSO_4 in straw are the main sources of sulfur. As the main component of coal gangue, Al_2O_3 can prevent the sulfur element in the straw from being decomposed and discharged into the air with the high-temperature combustion of the thermal expansion cracking agent. This shows that the use of straw in thermal expansion cracking agent has environmental protection.

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